



Inactivation of Bacteria *E. coli* and photodegradation of humic acids using natural sunlight

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ABSTRACT

In this work, the disinfection of bacteria *Escherichia coli* and degradation of humic acids, using sunlight, sunlight + TiO₂ (Degussa P25) in suspension or TiO₂ supported on Ahlstrom paper (NW10) fixed around concentric tubes inside the photoreactor, were investigated in a pilot plant. The inactivation of bacteria *E. coli* proved to be more efficient (only 1 kJ_{UV}/L for 5-log decrease in concentration) when using sunlight and TiO₂ in suspension. However, true disinfection was not achieved under the conditions reported in this work. A first-order model was able to fit the photocatalytic deactivation of *E. coli* ([TiO₂] = 50 mg/L) with an inactivation rate constant of 8.21 L/kJ. A Langmuir–Hinshelwood-like model was successfully applied for modelling photolysis and supported-TiO₂ photocatalysis of bacteria *E. coli*, considering an initial latency period, a classical log-linear behaviour and a tail region. The effect of the flow rate between 5 and 15 L/min was negligible in the inactivation of *E. coli* in the presence of sunlight and supported TiO₂. The inactivation rate constant increased with the initial concentration of *E. coli*. Almost no bacterial regrowth was observed in dark conditions during 24 h after illumination of *E. coli* suspension until complete deactivation. The humic acids (HA) degradation was also investigated by solar photocatalysis with suspended and supported TiO₂ and exposure to sunlight-only, in a CPC photoreactor. Supported-TiO₂ photocatalysis of HA originated 70% concentration reduction after Q_{UV} ≈ 14 kJ/L, whereas only 20% reduction was obtained by photolysis and slurry photocatalysis. First-order kinetic constants of 0.088 and 0.010 L/kJ were obtained, respectively, for suspended and supported TiO₂.

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1. Introduction

Water in sufficient quantity and good quality is essential for life. However, at the beginning of the year 2000 one sixth of the world's population, 1.1 billion people, was without access to improved water supply and many more lacking access to safe water [1]. Drinking-water of bad quality leads to a high risk of water-borne diseases such as diarrhoea, cholera, typhoid fever, hepatitis A, amoebic and bacillary dysentery and other diarrhoeal diseases. Each year 4 billion cases of diarrhoea cause 2.2 million deaths, mostly among children under the age of five [2].

Collection, treatment, storage and distribution of drinking-water involve deliberate additions of numerous chemicals to improve the safety and quality of the finished drinking-water for consumers. In addition, water is in constant contact with pipes, valves, taps and tank surfaces, all of which have the potential to impart additional chemicals to the water. The most commonly used techniques for water disinfection are chlorination and

ozonation [3]. Chlorine is widely used as main disinfectant, however there is the risk caused by the formation of chlorinated by-products such as trihalomethanes (THMs) and other total organohalides resulting from the reaction of chlorine with organic matter [4]. They also give drinking-water an unpleasant taste [5,6]. When used for irrigation, chlorine is often phytotoxic [7]. Other existing technologies, such as ozone and UV disinfection are clearly of very difficult implementation in rural areas [6]. Montgomery and Elimelech [8] report that overall water service coverage in rural areas is rather low, as a result of many factors (technological, cost, maintenance, social, cultural logistic, education, etc.).

Humic substances, mainly humic acids (HA), constitute the major fraction of natural organic matter in water supplies. They impart a brown/yellow colour to the water [9], can complex with metals [10] and organic pollutants, such as pesticides [11], and most significantly are precursors of mutagenic halogenated compounds formed in water after chlorination [12]. HA are normally eliminated from water before chlorination by coagulation with aluminium sulphate and filtration. The main disadvantages of this process are the production of residual sludge with high aluminium concentration and the need of high quality monitoring of aluminium concentration in treated water [13].

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Sunlight has been used as an agent for water disinfection in rural areas of poor countries which are among the sunniest in the world. The solar drinking-water disinfection process called SODIS [<http://www.sodis.ch/>], have gained support in recent years, mainly in rural areas [14]. The sunlight disinfection mechanism has been attributed to the heating effect and the production of reactive oxygen species by UV-A photosensitization of oxygen with the water [15]. However, the SODIS treatment efficiency can be highly affected by water turbidity, low irradiation intensity and regrowth of bacteria after the solar treatment, probably due to photo-repair mechanisms [16–18].

The combination of sunlight and a photocatalyst may be a promising option for areas with insufficient infrastructures but high yearly sunshine. This relatively new “Advanced Oxidation Technology” (AOT) is “clean”, low-cost, and can offer additional advantages in a wide range of applications. The typical photocatalytic technology is based on the interaction of light with suspended semiconductor nanoparticles (TiO_2) to produce highly oxidative species (i.e. the hydroxyl radical, HO^\bullet) from the adsorbed water. Such reactive oxygen species (ROS) destroy a large variety of co-adsorbed chemical pollutants and inactivate waterborne microorganisms [19,20]. Photocatalysis using TiO_2 semiconductor particles works in the UV-A region of the solar spectrum and is being increasingly used in AOT for water treatment with the hydroxyl radical [21].

A UV-A lamp (Radium Suprablack, HBT 125 W) with a very well defined emission peak at 365 nm was used for the photocatalytic disinfection of bacteria *Escherichia coli* using commercial titanium dioxide (Degussa P25) [22]. It was verified that the chemical composition of the water strongly affects the efficiency of the disinfection process. For example, low concentrations of humic substances inhibit the disinfection process, whereas the same concentration of sucrose does not affect at all.

Photocatalytic disinfection of *E. coli* K12 in water has been studied by Sichel et al. [23] in a pilot plant with 0.41 m^2 of compound parabolic collectors (CPC). The photocatalytic disinfection of *E. coli* with an initial concentration of 10^6 CFU/mL was complete after 90 min in the CPC reactor using TiO_2 immobilized on Ahlstrom paper (KN47). The photocatalytic disinfection was found to be more efficient at lower flow rates and approximately 99% of bacterial inactivation was shown to be caused by this mechano-osmotic dark inactivation.

Rincón and Pulgarin [18] verified an increase of *E. coli* concentration after illumination of bacteria without TiO_2 , however in the presence of TiO_2 , the decrease of bacteria continues in the dark, and no regrowth was observed within the following 60 h. The extension of this “residual disinfection effect” was dependent on the light intensity (400 or 1000 W/m^2) applied during illumination time.

Wiszniewski et al. [24] studied the photocatalytic decomposition of humic acids on TiO_2 and observed that HA are adsorbed on TiO_2 by carboxylate groups at acidic pH. It was obtained 88% of TOC removal after 6 h of irradiation (solar box ATLAS SUNTEST CPS+ simulating natural radiation) with an optimum TiO_2 loading of 1.0 g/L . Eggins et al. [25] studied the photocatalytic (0.1% (w/v) TiO_2 suspension) treatment of humic substances in drinking-water using a 250 W medium pressure mercury lamp and approximately 12 min were necessary to reduce the humic acid concentration by half (100 mg/L); however 50% mineralization took 60 min. Some of the intermediates of reaction were highly fluorescent.

Different types of inactivation empirical models have been used to describe the disinfection profiles over different types of microorganisms, photoreactors and operational parameters, based on thermal inactivation models [23], such as, Weibull type models [26], biphasic models with [27] or without shoulder [28], log-linear [29], log-linear + tail [30], log-linear + shoulder [30] and log-

linear + shoulder + tail [30] models. In this work we will attempt to apply a new inactivation model based on the reaction scheme of the series of events for bacterial inactivation first proposed by Severin et al. [31]. The simplified inactivation model has three parameters with physical meaning, allowing the interpretation of the disinfection results and evaluation of the influence of different process variables.

The objective of this work was to study in a pilot-scale plant using compound parabolic collectors the disinfection kinetics of bacteria *E. coli* and degradation of humic acids using sunlight without or with a catalyst (TiO_2) in suspension or immobilized in an inert matrix.

2. Experimental methodology

2.1. Solar CPC photoreactor

The disinfection experiments were carried out under sunlight at the roof of the Chemical Engineering Department, Faculty of Engineering, University of Porto (Portugal, local latitude $41^\circ 11' \text{N}$, longitude $8^\circ 42' \text{W}$), using compound parabolic collectors from Ao SOL, Energias Renováveis, Ltd. (Portugal) supported by an aluminium structure developed by Ecosystem-Environmental Services, S.A. (Barcelona, Spain) (Fig. 1). The solar collector is constituted by one CPC unit (0.59 m^2) of four borosilicate tubes (Schott-Duran type 3.3, Germany, cut-off at 280 nm, internal diameter 50 mm, length 1000 mm and thickness 1.8 mm) connected by plastic junctions tilted 41° local latitude (Fig. 1). A 35 W photovoltaic cell provides electric energy, which is accumulated in a 2 V DC 35 Ah battery, for water recirculation between the recirculation tank and the CPCs using a centrifugal pump DANGER TEN-Swiftech. The intensity of solar UV radiation is measured by a global UV radiometer (ACADUS 85-PLS) mounted on the pilot plant at the same inclination, which provides data in terms of incident W_{UV}/m^2 . Eq. (1) allows to obtain the amount of accumulated UV energy ($Q_{\text{UV},n} \text{ kJ/L}$) received on any surface in the same position with regard to the sun, per unit of volume of water inside the reactor, in the time interval Δt :

$$Q_{\text{UV},n} = Q_{\text{UV},n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{V_t}; \quad \Delta t_n = t_n - t_{n-1} \quad (1)$$

where t_n is the time corresponding to n -water sample, V_t is total reactor volume, A_r is illuminated collector surface area and $\overline{UV}_{G,n}$ is the average solar ultraviolet radiation measured during the period Δt_n . All experiments were done from March to July 2008 in cloudy and sunny days. Fig. 2 presents the solar UV irradiance over time in clear sunny days of March, April, June and July. The results showed high UV irradiance, achieving maximum values of approximately 58 W/m^2 in July.

The pilot plant includes a 20 L-capacity recirculation tank and two polypropylene valves for flow rate regulation and samples collection and, an electric board for process control and UV data acquisition (LS3200 and MAC-3580, DESIGN Instruments, SA).

2.2. Catalysts

The heterogeneous photocatalytic experiments were performed in a slurry suspension of Degussa P25 TiO_2 catalyst ($[\text{TiO}_2] = 50 \text{ mg/L}$), 80% anatase and 20% rutile, surface area = $55 \text{ m}^2/\text{g}$, non-porous particles, average particles size = 30 nm and, with Degussa P25 TiO_2 coated on a paper matrix Type NW10 “Ahlstrom paper”, at a dose of 11.8 g/m^2 , using an aqueous dispersion of colloidal SiO_2 as inorganic binder transparent to UV radiation [32]. The sheets of paper were fastened around the total perimeter of the concentric PP support tube placed inside the photoreactor tubes. A total of 0.36 m^2 of paper

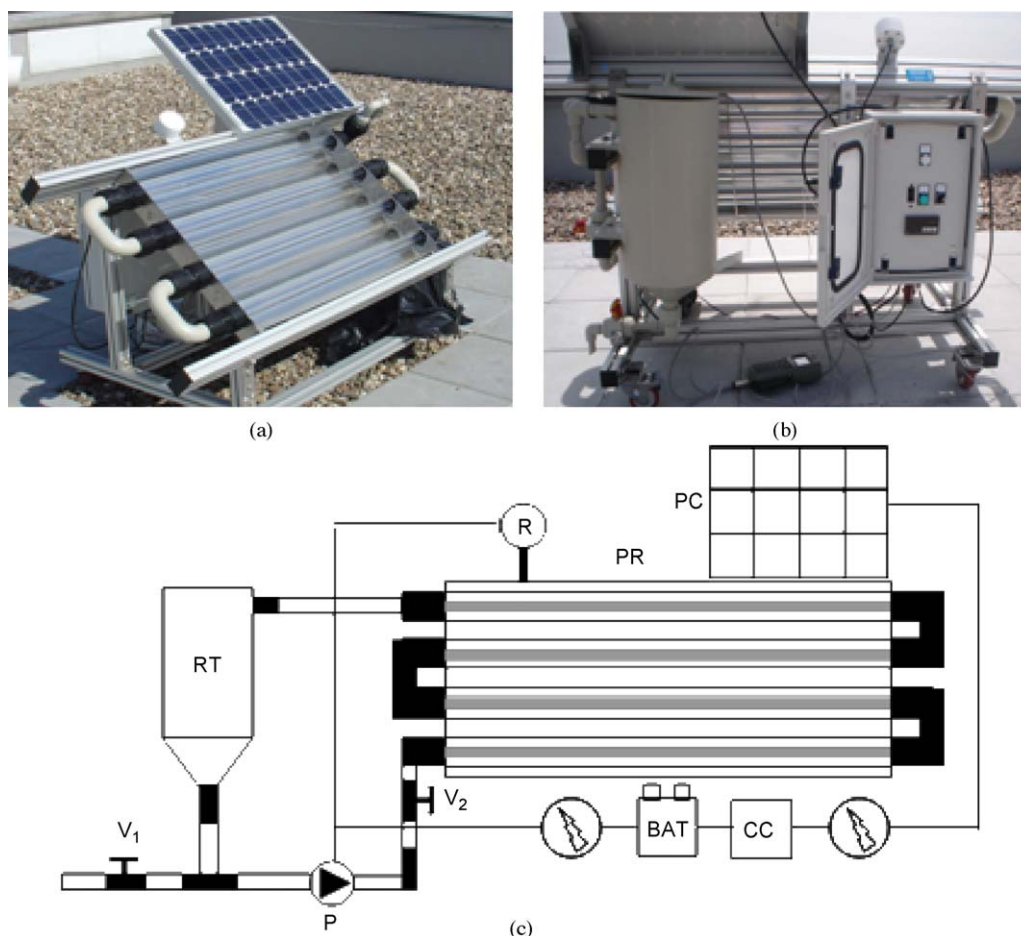


Fig. 1. Solar detoxification pilot plant. (a) Front view, (b) back view, (c) flowchart of the photoreactor; PR: photoreactor; PC: photovoltaic cell, R: radiometer; BAT: battery; CC: charge controller; P: pump; RT: recirculation tank; V₁: valve; V₂: flow rate controller.

was fixed on the four tubes of the CPC reactor. The Ahlstrom paper was previously washed three times with distilled water.

2.3. Bacterial strain, growth media and quantification

The bacterial strain used, *E. coli* DSM 1103, was inoculated into Nutrient Broth (NB) medium (Merck) and incubated at 37 °C under constant agitation and aerobic conditions during 15–16 h. After this, the basal equilibrium of bacteria was reached, yielding a concentration of 10⁹ CFU/mL. The suspensions were centrifuged at 3000 rpm

for 15 min and washed two times with saline solution (0.9% NaCl). Finally the bacteria pellet was re-suspended and diluted in the 15 L-tank to reach the initial cell concentration desired.

Filtration membrane methods (ISO 9308-1) were used for detection and enumeration of the bacteria, using Lauryl Sulphate Broth (Merck, Germany) for *E. coli*. All the material and solutions were sterilized before analysis.

2.4. Chemical analysis

Humic acid stock solution was prepared by dissolving a weighed quantity of humic acid sodium salt purchased from Aldrich in distilled water at 500 mg/L. The solution was filtered through glass microfibers paper (Fisherbrand MF 200). The dissolved organic carbon (DOC) was determined by using a TOC analyzer (Shimadzu, model 5000A). The UV–vis spectrum between 200–700 nm was recorded in a UNICAM HELIOS α spectrophotometer.

2.5. CPC reactor disinfection procedure

The recirculation tank was filled with 15 L of distilled water. Air bubbles were removed from the reactor and the flow rate of operation was selected. In the beginning of the experiments the reactor was covered to obtain dark conditions. A first control sample was taken in order to ensure the absence of water contamination. The bacteria suspension, or the humic acid concentrated solution, was added and mixed during 15 min to obtain a perfectly homogeneous solution. Then, a sample was

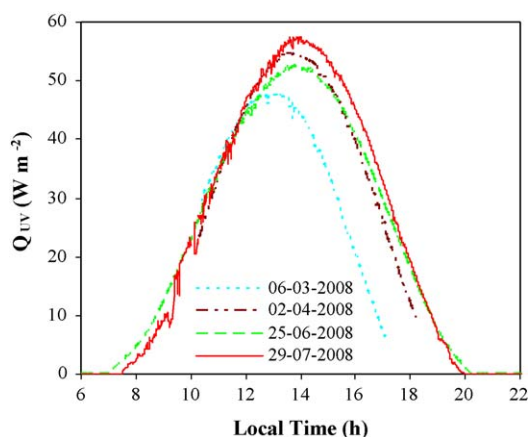


Fig. 2. Solar UV irradiance over time in clear sunny days of March, April, June and July of 2008 at FEUP (Portugal).

taken to determine the initial contaminant concentration. In the case of the experiments where sunlight-only and supported catalyst were used, the cover was removed and the experiment started taking samples at pre-defined times. As regards the photocatalytic experiments in slurry, after 15 min of solution homogenization, the TiO_2 particles were added to the recirculation tank, and the suspension was mixed during more 15 min in the dark. A new sample was taken in order to quantify the adsorption of humic acids or the inactivation of the bacteria in the presence of TiO_2 in darkness. Control tests were performed in dark conditions or in the presence of sunlight with or without catalyst.

3. Results and discussion

3.1. Disinfection of *E. coli* in synthetic waters

Fig. 3(a) presents the results of the inactivation of *E. coli* in distilled water, then avoiding interferences of specific ions and organic compounds, under dark conditions, sunlight-only, sunlight with TiO_2 in suspension and sunlight with supported TiO_2 . *E. coli* concentration under dark conditions remained almost constant throughout the experiment, but the addition of 50 mg/L of TiO_2 in suspension led to a small concentration decrease after 90 min, probably due to cell interaction with the surface of the catalyst. These results are in accordance with those obtained by Rincón and Pulgarin [33] in a Pyrex glass bottle under agitation (650 rpm). Similar results were also achieved by Sichel et al. [23] that obtained a 1-log decrease in concentration (initial concentration of 10^5 CFU/mL) using a 0.41 m^2 CPC pilot plant, with TiO_2 immobilized in KN47 paper matrix, operating at a flow rate of 10 L/min.

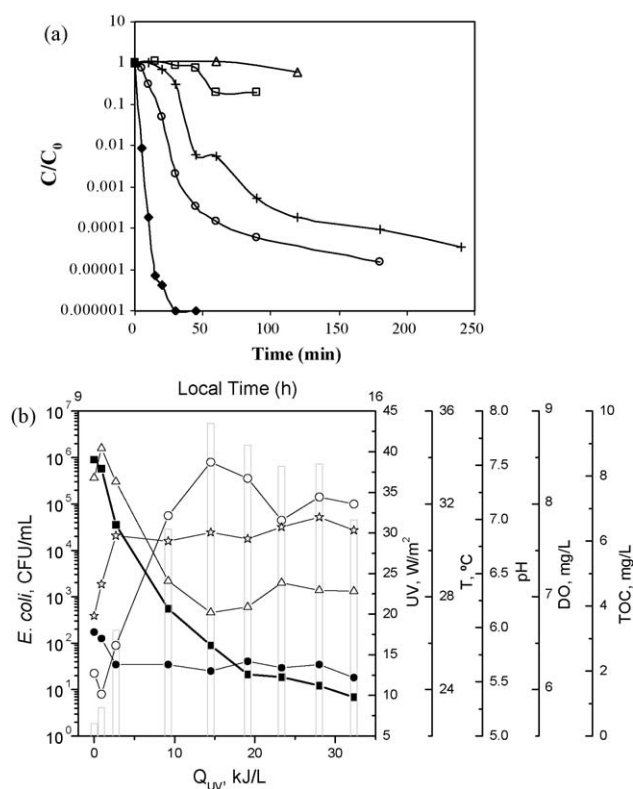


Fig. 3. (a) *E. coli* concentration over time in the CPC reactor during disinfection at different conditions. (–△–) Control in the dark; (–□–) TiO_2 without sunlight; (–○–) sunlight; (–◆–) TiO_2 in suspension with sunlight; (–+–) supported TiO_2 with sunlight. (b) Evolution of disinfection parameters as a function of accumulated UV energy, immobilized TiO_2 and $Q = 10 \text{ L/min}$: (–■–) *E. coli* concentration, (–△–) dissolved oxygen, (–○–) temperature, (□) UV, (☆) pH and (–●–) TOC.

The decreases in concentration of *E. coli* by solar photocatalysis were 6-log when using $[\text{TiO}_2] = 50 \text{ mg/L}$, 5-log for photolysis and only 4-log for photocatalysis with immobilized TiO_2 . The slower kinetics of *E. coli* inactivation with TiO_2 immobilized compared with photolysis can be attributed to the release of organic compounds that were detected during the experiments (Fig. 3(b)). These results agree with those obtained by Sichel et al. [34] that detected a faster CFU decrease in the sunlight-only experiments than in the TiO_2 -coated NW10 paper matrix experiments. Sichel et al. [34] also observed the leaching of organic substances from the NW paper matrix, based on TOC measurements. As shown in Fig. 3(b) the shape of the curve has an initial latency time, which indicates that at the beginning of the experiment, bacteria are only slightly affected by the phototreatment. This strong inhibition can be explained by several combined effects as radical scavenging, inhibition of the catalyst and absorption of light by the organic components, as well as competition between organic components and bacteria by hydroxyl radicals. Rincón and Pulgarin [33] also detected a negative effect on photocatalytic disinfection of *E. coli* in the presence of organic substances naturally present in water like dihydroxybenzenes isomers. The low activity of supported catalysts was also reported by Marugán et al. [22], since the bacteria must diffuse inside the porous structure of the supported matrix and reach the titania surface. In this situation the contact between TiO_2 and the microorganisms is limited to the TiO_2 crystals located in the external surface of the particles, which represents a small fraction of the semiconductor loading.

Fig. 4 shows the evolution of the *E. coli* concentration as a function of the amount of UV energy accumulated in the collector surface. It was necessary only 1 kJ of UV accumulated energy per liter of water to have a 5-log decrease in the concentration of *E. coli* using 50 mg/L of TiO_2 . However using sunlight-only or sunlight with immobilized TiO_2 , 4 and 16 kJ/L were required, respectively. Disinfection with sunlight-only reduces the need of water post-treatment by microfiltration or ultrafiltration. Those processes are very expensive, since the energy consumption and investment costs are high. The results obtained showed a good inactivation efficiency of *E. coli* in distilled water using sunlight-only.

Normally the microorganisms inactivation kinetic curves have three different regions: (i) an initial delay or smooth decay at the beginning of the reaction, usually called “shoulder” or latency phase, (ii) a log-linear inactivation region that covers most part of the reaction and (iii) a deceleration of the inactivation process at the end of the reaction, usually called “tail” and sometimes it can

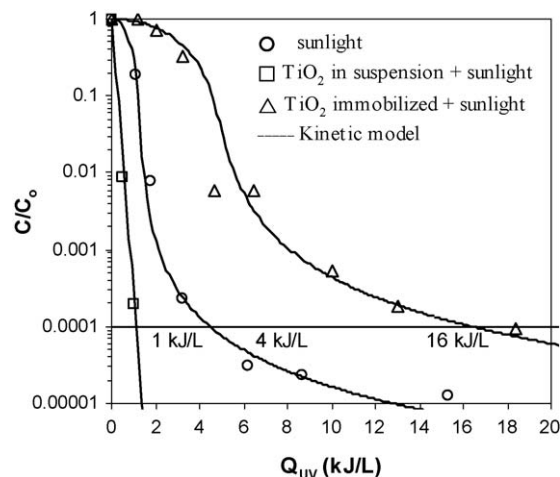


Fig. 4. Comparison of *E. coli* inactivation over time (accumulated UV energy) in the absence of catalyst, with TiO_2 in suspension and in supported form.

be observed a stationary phase which implies the existence of a more resistant subpopulation.

A first-order kinetic Chick–Watson model [35] (Eq. (2)) was successfully applied to describe the photocatalysis ($[\text{TiO}_2] = 50 \text{ mg/L}$), inactivation of *E. coli* (Fig. 4).

$$\frac{dC}{dt} = -k' \times C \Leftrightarrow \frac{dC}{dQ} = -k \times C \Leftrightarrow C = C_0 e^{-kQ} \quad (2)$$

where C represents the bacteria concentration at each time or accumulated UV energy during the solar reactor experiment (CFU/mL), C_0 is the initial bacteria concentration (CFU/mL), k is the bacteria inactivation rate constant (L/kJ) and Q is the accumulated radiation dose per liter of water (kJ/L).

Marugán et al. [22] presented a new inactivation model based on the reaction scheme of the series of events (Eq. (3)) for bacterial inactivation first proposed by Severin et al. [31].



where C_{undam} represents the undamaged population of bacteria, C_{dam} is a lump of bacteria in all intermediate levels of damage, C_{inact} is the population of inactivated bacteria and C_{prod} are the subsequent products of degradation formed from the oxidation of the organic components released to the medium after bacterial lysis. A Langmuir–Hinshelwood-like-inactivation equation was used to describe the reaction rate in the mass balance of the two species of interest, considering that a bacteria-catalyst–ROS interaction is required for the reaction to take place. Considering the inactivation rate constants, $k_1 = k_2 = k$, the pseudo-adsorption constants, $K_{\text{undam}} = K_{\text{dam}} = K$, which represent the interaction between the catalyst and the bacteria, responsible by the shoulder at the beginning of the reaction (however in the absence of catalyst, K can represent the interaction between the reactive oxidant species and bacteria) and, the inhibition coefficients, $n_{\text{undam}} = n_{\text{dam}} = n$, that essentially means that the reaction order with respect to the bacteria concentration is higher than one, we will obtain the following equations:

$$\frac{dC_{\text{undam}}^*}{dQ} = -k^* \frac{K^* (C_{\text{undam}}^*)^n}{1 + K^* (C_{\text{undam}}^*)^n + K^* (C_{\text{dam}}^*)^n} \quad (4)$$

$$\frac{dC_{\text{dam}}^*}{dQ} = k^* \frac{K^* (C_{\text{undam}}^*)^n - K^* (C_{\text{dam}}^*)^n}{1 + K^* (C_{\text{undam}}^*)^n + K^* (C_{\text{dam}}^*)^n} \quad (5)$$

where $C^* = C/C_0$, $k^* = k/C_0$ and $K^* = K \times C_0^n$. The solution of the system of ordinary differential equations (ODE's initial value problem) was accomplished using the solver LSODA [36]. This routine solves initial boundary problems for stiff or non-stiff

systems of first-order ODE's. For non-stiff systems, it makes use of the Adams method with variable order (up to 12th order) and step size, while for stiff systems it uses the Gear (or BDF) method with variable order (up to 5th order) and step size. The parameters were obtained by fitting the model to the experimental results ($C_{\text{undam}} + C_{\text{dam}}/C_0$) (initial conditions $t = 0$, $C_{\text{undam}}^* = 1$ and $C_{\text{dam}}^* = 0$) by minimizing the sum of the squares of the residues, i.e.,

$$\text{Min} \left\{ \sum_{i=1}^{\text{npts}} \left[\left(\frac{C_{\text{undam},i} + C_{\text{dam},i} - C_{\text{exp},i}}{C_0} \right)^2 \right] \right\} \quad (6)$$

where npts is the number of experimental points and C_{exp} is the concentration obtained experimentally. The minimization was carried out using a successive quadratic programming (SQP) algorithm.

Marugán et al. [22] used the L–H-like inactivation model to fit a large number of experiments of *E. coli* disinfection, evaluating the influence of titanium dioxide concentration, water chemical composition and the activity of silica-supported, TiO_2 , using a lab-scale photoreactor with a UV-lamp emitting at 365 nm.

The Langmuir–Hinshelwood-like-inactivation model was able to fit the inactivation experimental data by solar disinfection and solar TiO_2 immobilized photocatalysis as shown in Fig. 4. The inactivation constant rates for the three experiments at the same flow rate ($Q = 15 \text{ L/min}$) and similar initial bacterial concentration, indicate that the inactivation rate is higher for the photocatalysis with TiO_2 in suspension ($k = 8.21 \text{ L/kJ}$) than when using sunlight-only ($k^* = 1.66 \text{ L/kJ}$) and photocatalysis with immobilized TiO_2 ($k^* = 0.784 \text{ L/kJ}$).

pH, temperature and dissolved oxygen in the CPC reactor were measured during the disinfection process for the three systems. The initial pH of 5.5–6.0 stabilized quickly at 6.0–7.0. Rincón and Pulgarín [33] reported that *E. coli* inactivation rate was independent of the initial pH between 4.0 and 9.0. The initial temperature of approximately 22°C , normally increased throughout the experiment due to solar exposition, achieving maximum values of 38°C depending on the sunlight intensity. Rincón and Pulgarín [37] performed some experiments at different temperatures (23 and 45°C) and results showed a significant enhancement of the inactivation efficiency with the increase of the temperature. Dissolved oxygen decreased from the saturation value according to the water temperature, normally from 7 and 7.5 mg/L to 5.5– 6.0 mg/L . This oxygen decay is probably due to three reasons: (i) the increase of the water temperature, (ii) the consumption by the microorganisms and (iii) the consumption by photoactivated TiO_2 [38]. Considering the rise of the temperature from 22°C to approximately 38°C at the maximum, the decrease of oxygen can

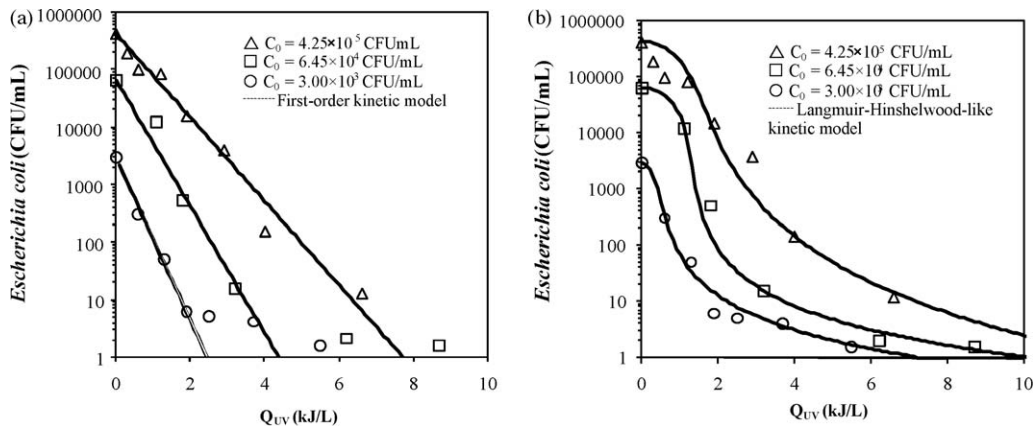


Fig. 5. Solar disinfection of *E. coli* at different initial concentrations and inactivation model fitting to the experimental data.

be caused principally by the temperature effect. However, O_2 consumption can also occur by reaction with UV + TiO_2 .

3.2. Influence of initial *E. coli* concentration on photolysis

To study the effect of the initial *E. coli* concentration on photolysis disinfection three experiments were carried out with 4.25×10^5 , 6.45×10^4 and 3.00×10^3 CFU/mL at 15 L/min. Fig. 5 shows that the latency phase decreases with the initial bacteria concentration. The shoulder effect can be attributed to self-defence mechanisms induced by UV in the stressed cells, which partially diminishes the effect of light during the first period of photo-treatment [37]. Craik et al. [39] showed also that if the bacteria concentration is high, a fraction of the bacteria could escape to UV exposure due to both shielding of microorganisms (high bacteria density) and poor mixing.

The results confirmed that more UV energy is needed for bacteria inactivation when the initial concentration is higher. An amount of 2, 4 and 7 kJ/L was required to reach the final concentration of 10 CFU/mL, respectively for initial *E. coli* concentrations of 3.00×10^3 , 6.45×10^4 and 4.25×10^5 CFU/mL. Sichel et al. [23] showed similar results for the inactivation of *E. coli*, where it was necessary 4 and 4.2 kJ/L to reduce the initial concentration of 10^5 to 10 CFU/mL and 10^7 to 90 CFU/mL.

Two inactivation models were applied to describe the experimental data. Fig. 5(a) and (b) shows the fitting curves obtained by the first-order model and Langmuir–Hinshelwood model, respectively. The first-order inactivation model was applied successfully to describe the inactivation of *E. coli* with TiO_2 in suspension and, as previously mentioned, it has been suggested by different authors to describe the inactivation of different microorganisms [18,40] (Fig. 4). However, the experimental data curves for the photolysis show three inactivation regions, as defined above, and the first-order model was not able to describe the experimental data. Fig. 5(b) shows that the L–H-like inactivation model is capable to fit the experimental data in all regions. The inactivation rate constants increase with initial bacteria concentration (Table 1) as expected, since the probability of interaction between the bacteria and the ROS is higher. After the log-linear region, the experimental curves show an extremely slow inactivation period, corresponding to the tailing region, which can be caused by one or several factors: (i) dead bacteria, and their excreted intracellular components, compete for photogenerated hydroxyl radicals, can form a screen to light penetration, leading to the protection of the remaining active sites, or the carbon source could facilitate the growth of some microorganisms [18,38]; (ii) surviving microorganisms could have a higher degree of resistance to both UV and oxidants photogenerated on TiO_2 [30]; (iii) some bacteria damaged by the hydroxyl radicals and UV light, could be repaired in dark periods inside the recirculation tank and fittings of the photoreactor [38].

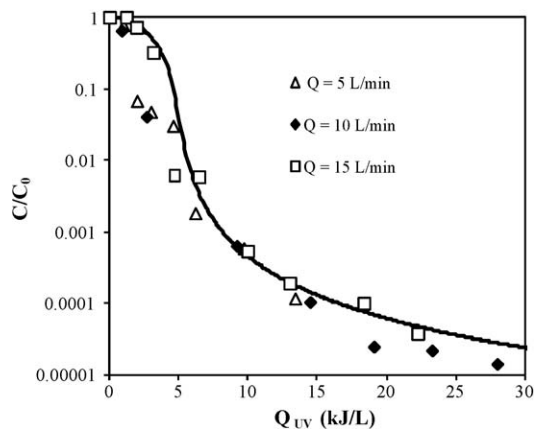


Fig. 6. *E. coli* concentration in the CPC reactor during supported- TiO_2 photocatalytic experiments at different flow rates; (—) Fitting of the kinetic model to the experimental data from the heterogeneous supported photocatalytic inactivation at 15 L/min.

3.3. Influence of flow rate on photocatalytic disinfection with immobilized TiO_2

The *E. coli* inactivation using the supported photocatalyst (NW10) was studied at three different flow rates, 5, 10 and 15 L/min. The obtained results, presented in Fig. 6, indicate similar efficiencies for bacteria inactivation for the three hydraulic regimes. The effect of flow rate on the bacteria inactivation can be attributed to different factors, such as, the mechanical stress promoted by the movement of the fluid in which bacteria are dispersed, the residence time of bacteria under solar radiation, the possibility of bacteria being adsorbed or reaching the supported catalyst, and the oxygen concentration in water. In the CPC reactor used in this work, the only oxygen source is the air contacting the water fall (ca. 20 cm) in the recirculation tank, which is open to the atmosphere. A higher flow rate will increase the oxygen concentration in water and better disinfection efficiencies should be expected, as detected by Fernandez et al. [41] using slurry TiO_2 catalyst. However, for immobilized catalyst, as used in this work, the main reaction constraint is the interaction between the catalyst surface and bacteria, once the surface area of the catalyst is lower and less oxygen is consumed throughout the reaction, which is attributed essentially to the increase of water temperature (Fig. 3(b)). Similar results were obtained by Gelover et al. [16] using a sol-gel immobilized (titanium dioxide) TiO_2 films over glass cylinders to disinfect total and fecal coliforms. Sichel et al. [23] showed a higher efficiency for the inactivation of bacteria *E. coli* using KN47 Ahlstrom paper for lower flow rates (2 L/min).

The Langmuir–Hinshelwood-like inactivation model was able to describe the experimental results obtained with the supported

Table 1

First-order and Langmuir–Hinshelwood-like inactivation model parameters for *E. coli* disinfection.

	First-order model				Langmuir–Hinshelwood-like model				
	Q (L min ⁻¹)	C _i (CFU mL ⁻¹)	k (L kJ ⁻¹)	R ²	k' (L kJ ⁻¹)	k × 10 ⁴ (CFU mL ⁻¹ L kJ ⁻¹)	K'	n	S _R ²
Sunlight	15	4.25×10^5	1.68	0.975	1.66	70.6	9.15	1.27	0.505
	15	6.45×10^4	2.54	0.966	1.63	10.5	102.3	1.55	2.6×10^{-4}
	15	3.00×10^3	3.27	0.993	4.83	1.45	9.32	1.57	2.84
Sunlight + TiO_2	15	1.05×10^7	8.21	0.991					
Sunlight + immobilized TiO_2	5	2.80×10^5	–	–	0.463	13.0	142.1	1.58	345.5
	10	8.95×10^5	–	–	0.784	70.2	113.4	1.58	4.4×10^{-2}
	15	3.85×10^4	–	–	0.434	16.7	83.3	1.52	3.2×10^{-2}

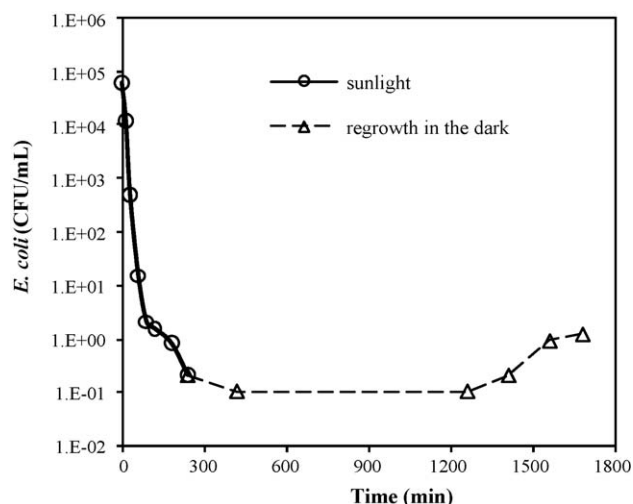


Fig. 7. Durability of solar disinfection (24 h in the dark).

catalyst at different flow rates (Fig. 6). The model parameters for the three experiments are very similar, although the inactivation rate constant for 10 L/min is slightly higher than for the other flow rates (Table 1). The inhibition coefficient values are very similar for the three experiments, 1.6, which means that the reaction order for the bacteria concentration is higher than 1, indicating a product inhibition phenomenon that seems to be independent of the flow rate. Unhappily, the activity for *E. coli* inactivation in supported catalyst is much lower than when using sunlight-only or TiO₂ in suspension, as indicated not only by the values of the inactivation rates constants but also by the pseudo-adsorption parameter (see Table 1), with exception for the experiment with an initial concentration of 6.45×10^4 CFU/mL. The inhibition coefficients values are very similar to those previously obtained for photolysis.

3.4. Durability of *E. coli* inactivation by sunlight

To study the durability of solar disinfection at field scale, 15 L of water, after an inactivation period with sunlight-only, were incubated in the dark with air bubbling. Fig. 7 shows that during the solar treatment in the absence of the catalyst, almost total inactivation was reached and a slight bacterial recovery was observed after 24 h, reaching a concentration of 1 CFU/mL. Rincón and Pulgarín [18,37] observed no bacterial growth (*E. coli* K12) after illumination of a contaminated TiO₂ suspension, however, without catalyst, illuminated bacteria recovered its initial concentration after 3 h in the dark. These results reveal that even if bacteria were not cultivable at the end of the phototreatment, some of them were actually not killed and recover their culturability after a period in the dark. These results were obtained in a lab scale photoreactor using a solar lamp (Hanau Suntest lamp).

3.5. Humic acids photodegradation

Humic acids photodegradation was performed using sunlight-only, sunlight + 50 mg/L of TiO₂ in suspension and sunlight + TiO₂ supported in Ahlstrom paper. The total organic carbon was used as a measure of the humic acids concentration. Humic acid concentration in the dark, without catalyst, remained approximately constant. However, with catalyst ([TiO₂] = 50 mg/L) a decrease of 16% on TOC was observed after 3 h of contact, which is related with the adsorption on the surface of the catalyst.

Fig. 8(a) and (b) shows the evolution of TOC, UV and other physical parameters, such as, pH, temperature, dissolved oxygen and

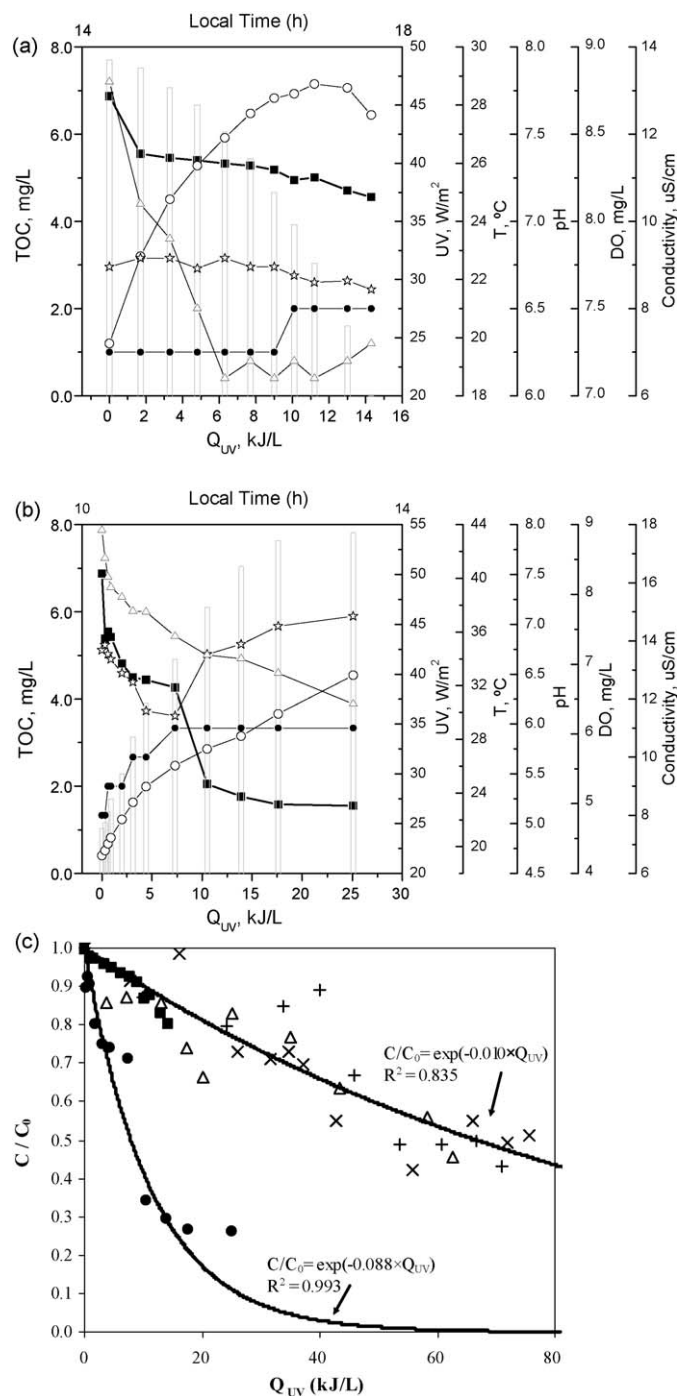


Fig. 8. Evolution of photodegradation parameters over accumulated UV energy. (a) Photolysis, (b) photocatalysis with [TiO₂] = 50 mg/L (—●—) TOC, (—△—) dissolved oxygen, (—○—) temperature, (—□—) UV, (—☆—) pH, (—●—) conductivity, (c) fitting of a first-order kinetic model to the experimental data of humic acids degradation: (■) sunlight (Q = 15 L/min); (●) sunlight and [TiO₂] = 50 mg/L (Q = 15 L/min); (+) sunlight and supported TiO₂ (Q = 5 L/min); (×) sunlight and supported TiO₂ (Q = 10 L/min); (△) sunlight and supported TiO₂ (Q = 15 L/min).

conductivity, as a function of the amount of UV energy accumulated per unit volume of fluid, during the photolysis and photocatalysis with [TiO₂] = 50 mg/L (initial concentration of humic acids ≈ 6.9 mg/L). Slurry photocatalysis of HA yielded a 70% concentration reduction after Q_{UV} ≈ 14 kJ/L, instead of 20% for photolysis and supported photocatalysis. The evolution of TOC during photocatalysis demonstrates the ability of TiO₂ to act as an efficient catalyst for HA photodegradation. The profiles presented in Fig. 8(c) are very similar

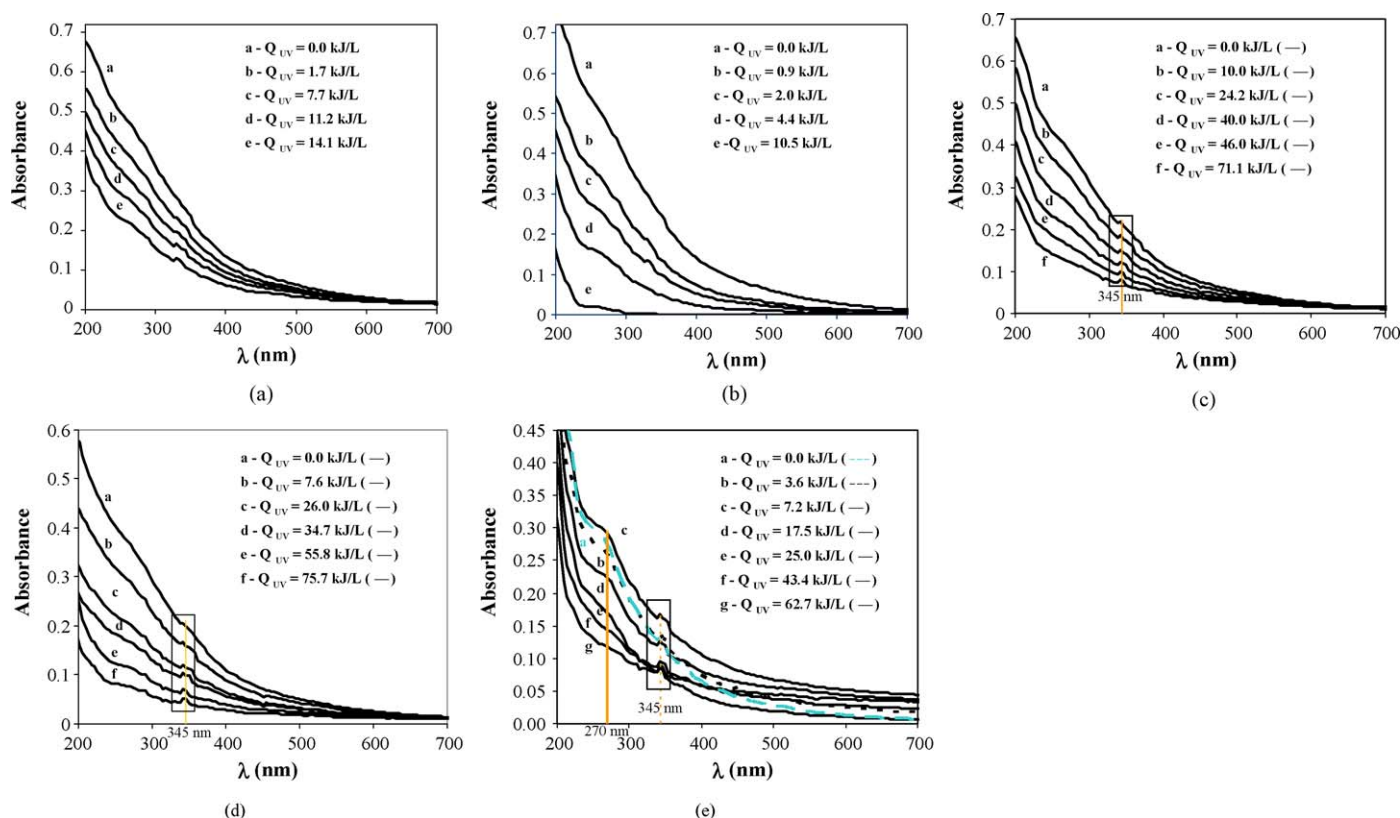


Fig. 9. UV-vis absorption spectra of commercial HA degradation: (a) sunlight ($Q = 15$ L/min); (b) sunlight + $[\text{TiO}_2] = 50$ mg/L ($Q = 15$ L/min); (c) sunlight + supported TiO_2 ($Q = 5$ L/min); (d) sunlight + supported TiO_2 ($Q = 10$ L/min); (e) sunlight + supported TiO_2 ($Q = 15$ L/min).

for the different flow rates, and the initial part of curve is analogous to that obtained when using sunlight-only.

The first-order model fitted curves are presented in Fig. 8(c). Kinetic constants of 0.088 and 0.010 L/kJ were obtained respectively for the system with TiO_2 in suspension and supported TiO_2 . The difference can be explained by difficult access to the TiO_2 particles by the humic acids, as described above for *E. coli* inactivation.

Fig. 9 depicts the UV-vis absorption spectra obtained in the experiments with HA solution. As expected the absorbance decreased as the reaction time increased for all situations, showing a rapid reduction of the absorbance for the photocatalysis with TiO_2 in suspension. Approximately 10.5 kJ/L was sufficient for the removal of the absorbance between 300 and 700 nm, as a result of the hydroxyl radicals production and consequent attack of the HA molecules. The UV-vis spectra from the experiments with the TiO_2 supported catalyst, show an absorbance peak at 345 nm, which increased with the reaction time, for all flow rates. This can be attributed to the formation of persistent intermediate compounds which are difficult to be degraded by this photocatalytic system. For the higher flow rate an absorbance peak at 270 nm appeared, resulting from HA degradation but disappeared after 62.7 kJ/L.

Wiszniewski et al. [24] studied the photocatalytic decomposition of humic acids on TiO_2 using a bench scale photoreactor with a solar box ATLAS SUNTEST CPS+ natural radiation simulator. The authors observed the presence of two domains of HA degradation kinetics: a first step, where a slight TOC decreased possibly due to the photodepolymerization of adsorbed HA on TiO_2 and a second one, where the photodegradation followed a pseudo-first-order kinetics. Organic intermediates were also detected and determined by HPLC. Approximately 300 min of irradiation time with $[\text{TiO}_2] = 1.0$ g/L are required for TOC reduction from 50 to 10 mg/L.

Eggins et al. [25] reported that 50% of humic acid was absorbed onto the titanium dioxide in the dark thereby reducing the initial readings by half in comparison with the original solution (100 mg/L). The degradation of the humic acid appeared to be complete after 50 min, as no absorbance at 254 and 400 nm and fluorescence was detected. However, both dissolved organic carbon (only 60% TOC efficiency) and carbon dioxide analysis suggested that mineralization was not complete. This reflects the fact that the humic acid is not degraded directly to carbon dioxide and water but via a series of intermediates, which have been detected during the phototreatment.

pH, temperature, dissolved oxygen and conductivity were also measured during the photodegradation of humic acids in the CPC reactor. As observed in the disinfection systems temperature increased from 20–22 °C to approximately 32–34 °C depending on the intensity of solar radiation during the experiment. The initial pH of the HA solution was around 6.5 and remained stable during photolysis (Fig. 8(a)), however a decrease in pH in the photocatalysis with TiO_2 in suspension was observed maybe due to intermediate acid compounds formation and then increased after 7.5 kJ UV/L until stable value of 7.0 (Fig. 8(b)). In the supported TiO_2 systems the pH remained approximately constant (6.5–7.0) throughout the experiments. The conductivity increased from 8 to 11 $\mu\text{S}/\text{cm}$ and 8 to 16 $\mu\text{S}/\text{cm}$ for the photodegradation experiments with TiO_2 in suspension and supported TiO_2 , respectively, as the result of the partial mineralization of HA releasing inorganic ions to the solution (Fig. 8(a) and (b)). The increase of the temperature or/and the O_2 consumption by photoactivated TiO_2 are responsible by the decrease of dissolved oxygen in water from approximately 8–9 to 6–6.5 (Fig. 8(a) and (b)).

4. Conclusions

The obtained results revealed that *E. coli* inactivation can be achieved by photolysis; however, the presence of TiO₂ in suspension accelerates the reaction. A non-empirical model (Langmuir–Hinshelwood), considering a simplified reaction mechanism, was successfully used to describe the *E. coli* inactivation. The inhibition coefficients allow to conclude that the bacteria inactivation reaction order is higher than 1. The interaction between the bacteria and the supported TiO₂ is the reaction constraint, reducing significantly the bacteria inactivation, as indicated by the values of the pseudo-adsorption constants. The release of organic matter from the support (paper matrix NW10) is also responsible by the absorption of UV light, radical scavenging and inhibition of the catalyst and, furthermore, may act as a nutrient supply for bacteria. The inactivation rate constants increase with the initial bacteria concentration, as expected, since the probability of interaction between the bacteria and the reactive oxygen species is higher. The impact of the mechanical stress associated with high flow rates is not significant for the interval of flow rates studied using the supported catalyst. After *E. coli* inactivation by photolysis no regrowth was observed during the subsequent 24 h in dark conditions, possibly due to the absence of a nutrient medium.

Humic acids degradation proved to be only efficient when using TiO₂ in suspension, due to the recalcitrant intermediates formed during the reaction. Slurry photocatalysis of HA yielded a 70% concentration reduction after $Q_{UV} \approx 14$ kJ/L, instead of 20% for photolysis and supported-TiO₂ photocatalysis. A first-order kinetic model was able to fit the experimental data of humic acids photodegradation. The kinetic constants are 0.088 L/kJ and 0.010 L/kJ, respectively, for suspended and supported TiO₂.

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